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Effects of charge on the structures and spin moments of Ni_{13} cluster*

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The structural stability and magnetic properties of the icosahedral Ni_{13}, Ni_{13}^{+1} and Ni_{13}^{-1} clusters have been obtained by utilizing all-electron density functional theory with the generalized gradient approximations for the exchange-correlation energy. The calculated results show that the ground states of neutral and charged clusters all favour a D_{3d} structure, a distorted icosahedron, due to the Jahn–Teller effect. The radial distortions caused by doping one electron and by doping one hole are opposite to each other. Doping one electron will result in a 1/2 decrease and doping one hole will result in a 1/2 increase of the total spin. Both increasing interatomic spacing and decreasing coordination will lead to an enhancement of the spin magnetic moments for Ni_{13} clusters.

Keywords: density functional theory, Jahn–Teller distortion, stable structures, spin magnetic moments
PACC: 3120A, 3640B, 2110K

1. Introduction

Microclusters have displayed a rapid development in experiment and theory since small atomic clusters are known to exhibit novel electronic, magnetic, optical, and chemical properties.[1,2] Transition-metal (TM) clusters, due to their unique physical and chemical properties,[3−5] have attracted much attention in scientific and technological fields. In cluster research, determination of geometry is the key to understand electronic and magnetic properties of clusters. Photoelectron spectroscopy (PES) experiment[6] is a valuable technique for exploring the electronic structure of mass-selected negative TM cluster ions. Several PES studies[7−9] on small TM clusters have been reported previously. The collision-induced dissociation experiment[10] on positive clusters can also provide much valuable, but usually indirect or incomplete information in predicting geometrical structures. In general, it is still difficult to directly detect the exact arrangements of such small clusters only by experimental approaches. Accurate theoretical calculations however can provide reliable information about the geometrical structures of small clusters. Researchers can predict some structures effectively by employing density functional theory (DFT).[11−13]

Nickel clusters seem to be one primary target of the investigations because of their catalytic and magnetic properties.[4,14,15] The cluster including thirteen atoms is the most studied aggregate, for 13 is a common magic number for many TM clusters. Electronic-structure studies on a Ni_{13} cluster have been carried out using a linear combination of atomic–molecular orbitals approach within the density functional formalism.[4] Structure studies on Ni_N (N = 2–13) clusters[16] have successfully verified quantum confinement[17] of 4s electrons in Ni smaller clusters and predicted that the ground state of Ni_{13} is indeed a distorted D_{3d} icosahedron. Spectroscopic evidence[8] was also provided for an icosahedral structure for Ni_{13}^{-1}. In order to clarify the effect of charge on structures and magnetic properties of Ni_{13} cluster, we have performed energy gradient and total-energy calculations by all-electron DFT with the generalized gradient approximations (GGA) for the exchange-correlation energy.[18]

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2. Computational details

Our calculations are based on DFT implemented in the DMol code,[19] with the all-electron spin polarized GGA for the exchange-correlation potentials.[20−22] We choose the non-local BLYP potential, i.e. the Becke exchange functional in conjunction with the Lee–Yang–Parr correlation functional.[16] The inner orbitals such as 3 s and 3 p sometimes are important for the ground-state properties of nickel clusters. We choose a double-numerical basis with polarized functions, which freezes only the 1 s, 2 s, 2 p orbitals in the present study. In the geometry optimization, the energy gradient and atomic displacement converge to 1×10^{-4} Hartree/Bohr and 1×10^{-5} nm respectively. The charge density converges to 1×10^{-3}e/nm^3, which corresponds to a total energy convergence of 1×10^{-5} eV.

The 3d open shells provide TM clusters with a complicated electronic structure, and consequently challenge the theoretical determination of their structures. Unlike the bulk phase, clusters with a given size can assume many structural forms corresponding to a multitude of local minima in the potential energy hyper-surface and there are abundant isomers with very close-lying energies. According to Jahn–Teller theory,[23] a nonlinear electronic system, which has orbital electronic degeneracy and high symmetry, is unstable, especially those systems where the highest occupied molecular orbital (HOMO) is not fully occupied. The Jahn–Teller distortions, which lower the structural symmetry, could help determine the ground states of small clusters. In searching the ground states, we have specified that symmetry should be used in order to obtain more information and save the calculation time.

3. Results and discussion

The four structures I_h, D_{5d}, D_{3d}, and D_{2h}, all belong to icosahedral structures. Only I_h is a regular icosahedron; all the others are relaxed icosahedrons. To reveal the stability of charged Ni_{13} clusters, we have investigated the optimal geometry and total spin of Ni_{13}, Ni_{13}^{+1} and Ni_{13}^{-1} with I_h, D_{5d}, D_{3d}, and D_{2h} symmetries. Figure 1 displays the configuration of the Ni_{13} cluster.

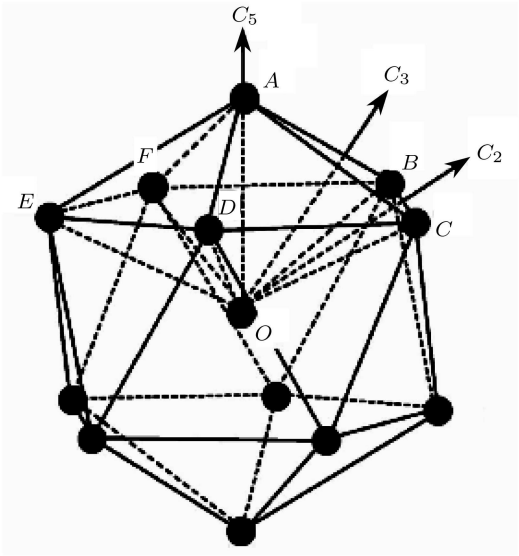


Fig.1. Structural sketch of Ni_{13} cluster. Balls symbolize the atoms, and some atoms are labelled by letters *A, B, C, D, E, F,* and *O*. The symbol of C_5, C_3, and C_2 denote the main axes in the clusters with the D_{5d}, D_{3d}, and D_{2h} symmetries, respectively.

The results have been summarized in Tables 1 and 2. The binding energy of a cluster system is defined as $E_b = E_{tot} - E_{sum}$, in which E_{tot} is the total energy of the cluster and E_{sum} is the sum of the energy of all free atoms in the cluster.

From the results shown in Table 1, we can see that the configuration with D_{3d} symmetry has the lowest binding energy for both neutral and charged clusters. The I_h symmetry has the highest binding energy, which is about 0.26–0.66 eV higher than that of the other configurations. The difference of binding energy between the D_{3d} and D_{2h} (or D_{5d}) configurations is less than 0.2 eV, which is less than 0.2% of the system binding energy. Therefore, it is reasonable to regard the D_{5d}, D_{3d}, and D_{2h} structures as degenerate isomers. The results of the binding energy reflect the complexity of TM clusters: there are many low-lying states with very close energies. From the analysis above, we can find that the cluster with high symmetry is not always more stable than that with low symmetry. High symmetry clusters, such as Ni_{13} with I_h symmetry, have heavy degeneracy and the Jahn–Teller effect is noticeable. Furthermore, doping one electron makes the binding energy lower 0.5–1.0 eV, and doping one hole results in a 5 eV increase of the binding energy. The results show that doping one electron could enhance the atomic bonding and the stability of Ni_{13} cluster.

Table 1. Calculated results for different structures of the Ni_{13} icosahedral cluster, including binding energy E_b, the HOMO state, the energy difference ΔE between the HOMO and the lowest unoccupied molecular orbital, the electron occupation number n in the HOMO, the total spin S, the atomic magnetic moment μ_O, μ_A, μ_B, μ_D and subscripts O, A, B, and D represent the sites in Fig.1, and the mean magnetic moment per atom $\bar{\mu}$, the mean atomic magnetic moment of surface atoms $\bar{\mu}_{surface}$, and the mean bond length between surface atoms $\bar{l}_{surface}$.

Sym	E_b/eV	HOMO	ΔE/eV	n	S	$\bar{\mu}/\mu_B$	$\bar{l}_{surface}$/nm	μ_O/μ_B	μ_A/μ_B	μ_B/μ_B	μ_D/μ_B	$\bar{\mu}_{surface}/\mu_B$
I_h	−52.05962	HU	0.195	3	4	0.615	0.24970	−0.472	0.706	0.706	0.706	0.706
I_h^{-1}	-53.0055	HU	0.195	4	3.5	0.538	0.24942	−0.630	0.636	0.636	0.636	0.636
I_h^{+1}	−46.9932	HU	0.137	2	4.5	0.692	0.25074	−0.405	0.784	0.784	0.784	0.784
D_{3d}	−52.71943	A2U	0.124	1	4	0.615	0.25018	0.492	0.626	0.626	0.626	0.626
D_{3d}^{-1}	−53.46374	A1G	0.078	1	3.5	0.538	0.25005	0.492	0.552	0.522	0.562	0.542
D_{3d}^{+1}	−47.62864	EU	0.106	2	4.5	0.692	0.25141	0.273	0.747	0.747	0.707	0.727
D_{5d}	−52.71926	A2U	0.112	1	4	0.615	0.25020	0.492	0.633	0.625	0.625	0.626
D_{5d}^{-1}	−53.26661	E1G	0.05	2	3.5	0.538	0.24984	0.449	0.604	0.534	0.534	0.546
D_{5d}^{+1}	−47.56391	E1G	0.108	2	4.5	0.692	0.2520	0.168	−0.719	−0.773	−0.773	-0.764
D_{2h}	−52.44182	B1U	0.229	1	4	0.615	0.25042	−0.335	0.695	0.695	0.695	0.695
D_{2h}^{-1}	−53.45806	AG	0.074	1	3.5	0.538	0.25004	0.491	0.521	0.577	0.529	0.542
D_{2h}^{+1}	−47.53889	B3U	0.079	1	4.5	0.692	0.25206	−0.347	0.812	0.788	0.737	0.779

In the following, we discuss the effect of the doping of electron or hole on the spin moment of Ni_{13} cluster. A Mülliken spin population analysis indicates that the additional charge makes the spin moment altered. For all structures investigated here, doping one electron will result in a 1/2 decrease of the total spin of the cluster and doping one hole will result in a 1/2 increase of the total spin of cluster, which is similar to the case in Ti_{13} cluster.[22] It is the reason that doping one electron in Ni_{13} cluster makes the number of unpaired electrons reduce and doping one hole makes the number of unpaired electrons increase as shown in Fig.2.

From Table 1, we can also see that the central atoms of both the neutral and the charged clusters have moment lower than the mean atomic magnetic moment of surface atoms. This is in agreement with the theoretical conclusions that the moment is governed by local coordination, and large coordination weakens magnetic moment.[24,25] This phenomenon can be simply understood from the filling of 3d orbitals. The large coordination of the central Ni atom results in the enhancement of the overlap of 3 d orbitals with those of other apex Ni atoms. Such an effect can reduce the exchange splitting of 3 d orbitals and consequently weaken its magnetism. From Tables 1 and 2, we can also find out that surface sites with different local environments have different local magnetic moments and, when local coordination is identical, the local magnetic moments of surface atoms will vary with surface interatomic spacing. For example, in D_{5d} structure the surface interatomic spacing of A site is larger than that of B site and the comparison of their magnetic moments shows the same pattern, that is, $\mu_A > \mu_B$. Another example is that, in D_{3d} structure, A site have a smaller surface interatomic spacing than D site and the comparison of their magnetic moments also shows the same pattern: $\mu_A < \mu_D$. The contraction in interatomic spacing reduces the magnetic moment.

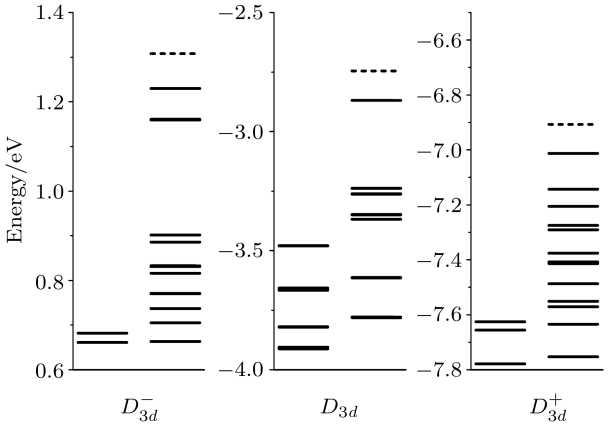


Fig.2. Energy levels of the ground state of Ni_{13} neutral and charged clusters. Solid lines refer to occupied states. The dashed lines refer to unoccupied states. And for a certain cluster, the solid and dashed lines on the left denote the spin-up state and those on the right denote the spin-down state.

Table 2. Calculated bond lengths (in nm) in Ni_{13}, Ni_{13}^{+1} and Ni_{13}^{-1} clusters with different symmetries. Symbols I_h^{+1} and I_h^{-1} have same symmetry with I_h and other symbols in the first column are defined in the same way. *O, A, B, C, D* and *E* represent the sites in Fig.1.

Sym	OA	OB, OC	OD, OF	OE	AB, AC	AD, AF	AE	BC	CD, FB	DE, EF
I_h	0.2375	0.2375	0.2375	0.2375	0.2497	0.2497	0.2497	0.2497	0.2497	0.2497
I_h^{-1}	0.2372	0.2372	0.2372	0.2372	0.2494	0.2494	0.2494	0.2494	0.2494	0.2494
I_h^{+1}	0.2385	0.2385	0.2385	0.2385	0.2507	0.2507	0.2507	0.2507	0.2507	0.2507
D_{3d}	0.2379	0.2379	0.2379	0.2379	0.2502	0.2501	0.2502	0.2501	0.2502	0.2502
D_{3d}^{-1}	0.2378	0.2378	0.2378	0.2378	0.2465	0.2526	0.2499	0.2465	0.2526	0.2487
D_{3d}^{+1}	0.2389	0.2389	0.2393	0.2393	0.2480	0.2529	0.2523	0.2480	0.2529	0.2509
D_{5d}	0.2380	0.2380	0.2380	0.2380	0.250	0.250	0.250	0.2501	0.2501	0.2501
D_{5d}^{-1}	0.2363	0.2379	0.2379	0.2379	0.2505	0.2505	0.2505	0.2509	0.2509	0.2509
D_{5d}^{+1}	0.2346	0.2406	0.2406	0.2406	0.2494	0.2494	0.2494	0.2527	0.2527	0.2527
D_{2h}	0.2382	0.2381	0.2381	0.2382	0.2493	0.2493	0.2551	0.2551	0.2492	0.2493
D_{2h}^{-1}	0.2376	0.2361	0.2397	0.2376	0.2501	0.2530	0.2470	0.2480	0.2493	0.2530
D_{2h}^{+1}	0.2416	0.2394	0.2382	0.2416	0.2524	0.2515	0.2532	0.2462	0.2535	0.2515

Now we discuss the effects of additional charge on bond length between surface atoms ($\bar{l}_{\rm surface}$) and the mean atomic magnetic moment of surface atoms ($\bar{\mu}_{\rm surface}$). For a certain symmetric cluster, from doping one electron to neutral to doping one hole, $\bar{l}_{\rm surface}$ increases by degree. Compared with the neutral cluster, doping one electron makes the $\bar{l}_{\rm surface}$ shortened by 0.000136–0.00036 nm and the $\bar{\mu}_{\rm surface}$ weakened by 0.7–0.153 $\mu_{\rm B}$; and doping one hole makes the $\bar{l}_{\rm surface}$ extended by 0.00123–0.019 nm and the $\bar{\mu}_{\rm surface}$ strengthened by 0.08–0.14 $\mu_{\rm B}$. This is just in accordance with the conclusion in cobalt clusters:[26] the shorter the $\bar{l}_{\rm surface}$, the smaller the $\bar{\mu}_{\rm surface}$.

Table 2 presents the calculated bond lengths in Ni_{13}, Ni_{13}^{+1} and Ni_{13}^{-1} clusters. We can classify the bonds (see Fig.1) as the perpendicular and the parallel according to their orientation relative to the main axis of the group. The characteristic perpendicular bonds for the I_h, D_{3d}, D_{5d}, and D_{2h} structures are $\{BC\}$, $\{AB\}$, $\{BC\}$, and $\{OD, BC\}$, respectively; the characteristic parallel bonds for the I_h, D_{5d}, and D_{2h} structures are $\{OA\}$, $\{OA\}$, and $\{AE\}$, respectively. For the I_h structure, it can be found that the additional electron in the negatively charged cluster has made the surface atoms move towards the centre atom and the bond lengths between apex and centre atom (i.e. OA, OE, OD etc.) decrease, which cause the structure more compact and the binding energy lower almost by 1 eV. In contrast, in the positively charged cluster the surface atoms all depart from the centre atoms along the icosahedral radius, which makes the structure less compact and the binding energy increases by almost 5 eV. Obviously, the way of the variation of bond lengths along the radial in other symmetries is similar to the case in the I_h structure, i.e. doping one electron makes the structure contracted radially and the effect of doping one hole is just the reverse. For the charged D_{2h} structure, the parallel bond AE shows remarkable variations as compared with those in the neutral D_{2h} structure, and these variations in the negative D_{2h} structure are also opposite to those in the positive D_{2h} structure. However, for the bond lengths of the perpendicular bond BC, the effect of positive charge is the same as that of negative charge. The way of the variation of perpendicular bond lengths in the D_{3d} structure is similar to the case in the D_{2h} structure. For D_{5d} structure, the additional electron has made the parallel bond OA decrease and perpendicular bonds (e.g. BC etc.) increase. The above results clarify the effect of additional charge on the atomic structure of Ni_{13} cluster.

4. Summary

The structural stability and magnetic properties of the icosahedral Ni_{13}, Ni_{13}^{+1} and Ni_{13}^{-1} clusters have been investigated based on all-electron DFT with the spin polarized GGA for the exchange-correlation potentials. It is found that the ground states of neutral and charged 13-atom clusters all favour a D_{3d} structure, a distorted icosahedron. Doping one electron could enhance the atomic bonding and the stability of Ni_{13} clusters. The radial distortions caused by doping one electron and doping one hole can be opposite to each other. The additional charge produces sig-

nificant effect on the spin moments of Ni_{13} cluster: doping one electron will result in a 1/2 decrease and doping one hole will result in a 1/2 increase of the total spin. Interatomic spacing and coordination are also two effects in determining magnetic moment of the clusters: both increasing interatomic spacing and decreasing coordination will lead to the enhancement of the magnetic moments.

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